12

#### **EUROPEAN PATENT APPLICATION**

(2) Application number: 87303687.5

2 Date of filing: 27.04.87

(a) Int. cl.4: **B 41 M 5/035**D 06 P 5/00

30 Priority: 29.04.86 GB 8610429

Date of publication of application: 04.11.87 Bulletin 87/45

Designated Contracting States:
 AT BE CH DE ES FR GB GR IT LI NL SE

(7) Applicant: Sericol Group Limited 24 Parsons Green Lane London SW6 4HT (GB)

(2) Inventor: Hester, Nigel Lewis 13 Pallet Way Shooters Hill Road London SE 18 (GB)

Representative: Claisse, John Anthony, Dr. 11 Evelyn Avenue Ruislip Middlesex, HA4 8AR (GB)

(54) Transfer compositions.

(g) Printing compositions for producing a heat transferable design on textiles or fabrics. The compositions consist of a thermoflowable polymer and a blocked isocyanate crosslinking agent flowable at temperatures at which the polymer flows. The blocking agent is removable by heating at a temperature at which the polymer flows, thereby producing a crosslinking agent for crosslinking the polymer. The compositions are substantially tack free at ambient temperatures.

Also provided are transfers for producing designs on textiles or fabrics, the transfers consisting of a temporary support with a design formed from a composition of the invention.

EP 0 244 181 A2

#### Description -

5

10

15

20

25

30

35

45

50

60

#### TRANSFER COMPOSITIONS

The present invention concerns printing compositions for the production of heat transferable designs on textiles by heat transfer printing.

Heat transfer printing utilizes a temporary support sheet, usually a coated paper, for example a siliconized parchment paper, with a design screen printed thereon. After drying the ink, the temporary support sheet is placed in direct contact with the textile article to be decorated, and transfer is effected using a heat transfer press. Predetermined heat and pressure are applied by this process, and the article plus support sheet is withdrawn after a preselected dwell time. Finally, the temporary support is peeled away, the design having been transferred to the article.

Advantages gained using a transferrable design compared with direct printing include:-

(1) The avoidance of textile manufacturers having to employ skilled printing operatives or to invest in expensive printing machinery,

(2) a reduction by retailers of stocks of preprinted goods, thereby saving on possible articles printed with redundant designs, and

(3) a greater freedom on the part of the purchaser to choose a preferred design for his garment.

Sufficient penetration of the ink film into the textile under heat transfer has hitherto required critical formulation of the ink so that the transferred design does not adversely affect the natural texture or 'hand' of the fabric. Vapour phase, or subliming technology has been successfully applied, and one method of this type is described in British Patent Specification 1433763.

Sublimation transfers are not generally suitable for wool or cellulosic materials such as cotton, due to inadequate fastness properties. Futhermore, it may not be suitable for additional heat treatment processess such as ironing or pleating, as further dye-sublimation may occur.

Another approach, described in British Patent Specification 1589292, utilizes the addition to the ink of up to 80% of a non-tacky, wax-like solid which melts at the operational temperature, thus effecting penetration of the ink film into the fabric. Transfers based on the addition of wax-like solids generally require an extra layer of a high melting point polymer to achieve maximum fastness. This is because the solid material added is non-reactive and it therefore remains essentially thermoplastic. Furthermore it is susceptible to leaching by washing and ironing and by dry cleaning processes.

Resistance to abrasion due to wear, washing, ironing, dry cleaning etc. can be achieved using inks based on a polymer which is inert to heat and hydrolysis, and which is insoluble in solvents encountered in dry cleaning processes. Polymers exhibiting such resistance properties are generally of high molecular weight and high melting point, and are insoluble, or only partially soluble, in the common organic solvents used in printing inks. Heat transfers produced using polymers of this type do not penetrate into the fabric because of their high melt viscosity at transfer temperatures. Designs produced using high molecular weight polymers in heat transfer generally produce non-penetrative labels when transferred, and these generally interfere with the natural texture of the material and in extreme cases, being on the surface of the fabric, they may crack as the textile is flexed.

According to the present invention there is provided a printing composition for producing a heat transferable design on a textile or fabric, the composition comprising a thermoflowable polymer and a blocked isocyanate crosslinking agent flowable at temperatures at which the polymer flows, the blocking of the agent being removable by heating the agent at a temperature at which the polymer flows to produce a crosslinking agent for crosslinking the polymer, the composition being substantially tack free at ambient temperatures.

The invention further provides a transfer for producing a design on a textile or fabric, the transfer comprising a temporary support member, and a heat transferable design thereon, the design being substantially tack free at ambient temperatures and being formed from an ink composition comprising a thermoflowable polymer and a thermoflowable blocked isocyanate crosslinking agent capable of flowing and being unblocked at a temperature at which the polymer flows, the unblocked agent being capable of crosslinking said polymer. A clear varnish of similar composition may also be employed as a primer coat to ease transfer or adhesive layer applied after the design layer.

The invention still further provides a method of producing a design on a fabric or textile, the method comprising applying a printing composition according to the invention to the fabric or textile and heating the composition so that the polymer and the blocked crosslinking agent flow, the blocked isocyanate crosslinking agent is unblocked, and the polymer and unblocked crosslinking agent react to produce a crosslinked polymer.

Compositions in accordance with the present invention can for example be in the form of an ink suitable for screen printing.

Designs produced using printing compositions of the invention can be applied to synthetic or natural fabrics.

When such designs have been heat transferred to a fabric, they have been found to be relatively unaffected by processes normally encountered during the life of garments having them thereon, for example abrasion due to wear, washing, ironing or dry cleaning etc. The cured polymer has been found to be tough enough to counter abrasion through normal wear and tear, and be able to withstand many cycles of washing and ironing.

#### 0 244 181

The present invention allows heat transfers to be produced which penetrate into the fabric but which also have good resistance properties. This is achieved by the combination of a heat softenable polymer having chemically reactive sites and a heat softenable isocyanate cross linking agent which reacts with functional groups of the heat softenable polymers under the conditions of heat transfer.

Heat transfers of the type produced using the present invention are generally referred to as 'filmless' or 'low feel' as the transferred ink film allows the material to which the designs are applied to retain its natural texture, i.e. 'drape' and 'handle'.

During heat transfer, the combination of polymer and crosslinker should have sufficiently low melting characteristics to allow penetration of the heat softened composition into the fibres of the material.

However, once the process of transfer is complete the polymer now being crosslinked exhibits the excellent resistance properties normally associated with polymers of higher molecular weight.

In general it is preferred that the thermoflowable polymer:-

DALVMED TYPE

(1) is low melting with melting preferably being in the range 80°C - 120°C

(2) has a high degree of chemical functionality, e.g. hydroxyl, carboxyl or amino groups; and

(3) is easily solvated by organic solvents commonly employed in screen printing compositions.

Examples of thermoflowable polymers which can be used in compositions of the present invention include:-

TVDTCAL

PULTMER TIPE	ITELONG	! OHE ! TOWNER! !		
2	MELTING RAN	GE	20	
Thermoplastic acrylics	95-115°c	Hydroxyl & Carboxyl	25	
Modified ketone resins	110-125°C	Hydroxyl	بحر	
Thermoplastic polyesters	115-125°C	Carboxyl		
Hard Resins, e.g. Ester gums	60-85°C	Carboxyl	30	
Thermoplastic epoxys	65-124°C	Hydroxyl	-	
Reactive polyamide	20-120°C	Amino		

Crosslinking agents which can be used include blocked polyisocyanates which are preferably solids with relatively low melting and unblocking temperatures. Melting point is preferably in the range from 80-120° C with unbocking temperatures preferably 100-200° C, and more preferably 115-170° C. The use of a polyisocyanate with a low unblocking temperature is particularly preferred so that the isocyanate moeity is unblocked under transfer conditions, the blocking agent then being vaporised and hence lost from the ink film during transfer. Dimethylpyrazole and butanediol are examples of blocking agents which can be used.

The melting ranges of the preferred blocked polyisocyanates are similar to those of the preferred polymers thereby assisting the latter to penetrate into the material. Furthermore the preferred solid form of the blocked crosslinking agent is soluble in organic solvents which are commonly encountered in screen printing compositions, e.g. aromatic hydrocarbons, glycol ethers, etc.

In order to ensure that as far as possible reaction between the functional groups of the polymer and the unblocked polyisocyanate proceeds to completion, a catalyst will usually be included. In a preferred embodiment of the present invention dibutyl-tin-dilaurate is used as a catalyst.

The conditions of transfer will in general be in keeping with current commercial practice. Typical heat transfer will take place at a temperature of from 150°C to 200°C and typical dwell times are of from 5 to 60 seconds.

The following Examples are given by way of illustration only. All parts are by weight unless otherwise stated. Examples 1 and 3 are of clear compositions used as the release layer. This layer is printed first onto a temporary backing sheet and it facilitates release of the design. It also gives additional protective properties to the design once transferred onto the material. The design can be one or more layers of ink manufactured by the incorporation of one or more pigments into a varnish such as in Examples 2 or 4. The so-produced inks and varnish are capable of being both printed and dried under normal procedures encountered in a printshop, for example existing printing machinery and jet driers.

Alternatively the clear composition can be applied after the design layer. The resulting transfers are then transferred onto natural and synthetic fabrics at 180-190°C for 15-20 seconds.

#### Example 1

65

60

10

15

35

45

FUNCTIONALITY

# 0 244 181

	*		Parts
5	:	Thermoplastic epoxy resin	22.6
_		Blocked polyisocyanate	16.1
		Thixotrope	5.8
. 10	•	Catalyst	0.2
		Silicone additive	0.5
	" · · · · · · · · · · · · · · · · · · ·	Glycol ether acetate solvent	54.8
15			
ñ		- N - 1	100.0
20	•		
20	Example 2		$A_{ij}$
			Parts
25		Thermoplastic epoxy resin	18.9
		Blocked polyisocyanate	13.5
		Phthalocyanine blue pigment	2.4
30		Talc	9.7
		Thixotrope	4.8
		Catalyst	0.2
35		Silicone additive	0.4
		Glycol ether acetate solvent	50.1
40			100.0
	•		
45	Example 3	•	
			Parts
		Modified ketone resin	25.1
50		Reactive polyamide resin	6.3
		Blocked polyisocyanate	15.5
		Thixotrope	9.4
. <i>55</i>		Catalyst	0.2
		Silicone additive	0.5
		Glycol ether acetate solvent	43.0
60		•	100.0

65

#### Example 4

* 0.000	Parts		
Modified ketone resin	19.3		5
Reactive polyamide resin	4.8		
Blocked polyisocyanate	11.9	•	
Phthalocyanine blue pigment	2.7		10
Talc	10.8	*	,,,
Thixotrope	7.2	2	
Catalyst	0.2		15
Silicone additive	0.5	*	
Glycol ether acetate solvent	42.6	*	

20

#### **Claims**

1. A printing composition for producing a heat transferable design on a textile or fabric, the composition comprising a thermoflowable polymer and a blocked isocyanate crosslinking agent flowable at temperatures at which the polymer flows, the blocking of the agent being removable by heating the agent at a temperature at which the polymer flows to produce a crosslinking agent for crosslinking the polymer, the composition being substantially tack free at ambient temperatures.

30

25

2. A composition according to claim 1, wherein the flowable polymer has hydroxy, carboxyl or amino groups.

\_\_

3. A composition according to either of the preceding claims, wherein the blocked crosslinking agent has blocked isocyanate groups, and the thermoflowable polymer has groups reactive with said unblocked isocyanate groups.

.

4. A composition according to any of the preceding claims, wherein the blocked crosslinking agent is unblocked at a temperature of from 115 to 170°C.
5. A composition according to any of the preceding claims, which includes a catalyst for the

40

crosslinking.

6. A transfer for producing a design on a textile or fabric, the transfer comprising a temporary support member, and a heat transferable design thereon, the design being substantially tack free at ambient temperatures and being formed from a printing composition comprising a thermoflowable polymer and a thermoflowable blocked isocyanate crosslinking agent capable of flowing and being unblocked at a

45

temperature at which the polymer flows, the unblocked agent being capable of crosslinking said polymer.

7. A transfer according to claim 5, wherein the design is produced from a composition according to any of claims 2 to 5.

8.. A transfer according to either of claims 6 or 7, having a release layer with the heat transferable design thereon.

50

9. A transfer according to either of claims 6 or 7, where the clear composition according to claims 2 to 5 is applied after the design layer.

10. A method of producing a design on a fabric or textile, the method comprising applying a printing composition according to any of claims 1 to 5 to the fabric or textile and heating the composition so that the polymer and the blocked isocyanate crosslinking agent flow, the blocked crosslinking agent is unblocked, and the polymer and unblocked crosslinking agent react to produce a crosslinked polymer.

55

11. A method according to claim 10, wherein the ink composition is applied using a transfer according to any of claims 6 to 9.

60

65

	i						•								
				•									٠.		4
			· .												
	4											* .	•		٠
					•		·			*					
		*				•									٠
	ÿ								-2.					·	
	J.			•			•								
	45	•									•				
														. •	
												•	•	•	-
. •					* : • *		*								•
				•				٠							
	\$													•	
									*						
													•		
**	· •													•	• :
•		,	e												
														•	
			•	• .					٠,			• •			
	٠.														
												•			
	٠.														
•	•			,						-(0					
					•										
	il.					•									
			•		· ·										
•	: .				. 5				•						
	.:									*(**		•			
							,								
	٠.										•	• 00			
					•			,							
							-								
											•				٠.
					•	•				1)1					
				*											
				. •							• • •				
					•										
														•	
			•		• •										
											*	•			
	.:														
										•	,			*.	
•	:														
	•										٠.	•			
.*													á.		
							•								•
	٠.		•												
									÷						•
•	:									· ·		٠			
•	:		•										•		
				•						•					•
				-											
							,			*					
										•					

## 12

## **EUROPEAN PATENT APPLICATION**

- (1) Application number: 87303687.5
- (5) Int. Cl.5: B41M 5/035 , D06P 5/00

- ② Date of filing: 27.04.87
- (3) Priority: 29.04.86 GB 8610429
- (3) Date of publication of application: 04.11.87 Bulletin 87/45
- Designated Contracting States:
   AT BE CH DE ES FR GB GR IT LI NL SE
- Date of deferred publication of the search report:
  02.05.90 Bulletin 90/18
- Applicant: Sericol Group Limited 24 Parsons Green Lane London SW6 4HT(GB)
- Inventor: Hester, Nigel Lewis13 Pallet WayShooters Hill Road London SE 18(GB)
- Representative: Claisse, John Anthony, Dr. 97 Portway
  Wells Somerset BA5 2BR(GB)

- (54) Transfer compositions.
- © Printing compositions for producing a heat transferable design on textiles or fabrics. The compositions consist of a thermoflowable polymer and a blocked isocyanate crosslinking agent flowable at temperatures at which the polymer flows. The blocking agent is removable by heating at a temperature at which the polymer flows, thereby producing a crosslinking agent for crosslinking the polymer. The compositions are substantially tack free at ambient temperatures.

Also provided are transfers for producing designs on textiles or fabrics, the transfers consisting of a temporary support with a design formed from a composition of the invention.

EP 0 244 181 A3

# European Patent Office

## EUROPEAN SEARCH REPORT

EP 87 30 3687

Category	Citation of document with indicati		Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
ĸ	CHEMICAL ABSTRACTS, vol. 88	, no. 7, 03 April	1-11	B41M5/035 D06P5/00
	Columbus, Ohio, USA			
	Tanaka, Kinji: "One liquid-	type thermosetting	1	
	inks for textile transfer p	rinting" & JP-A-52112		
ł	406 ; 20.09.1977	00070		
	page 66; column 2; ref. no. * abstract *	90978		
	GB-A-2095619 (MUSER)		1-3, 10,	
	* the whole document *		11	
	FR-A-2391859 (POLYMARK INTE	RNATIONAL LTD)	1-11	·
	* the whole document *			
	 CHEMICAL ABSTRACTS, vol. 10	4, 1986	1-3	er en
	Columbus, Ohio, USA			
	Taruya et al,: "Transfer pr liquid compositions" & JP-A		e .	
	Printing Co. Ltd) 06.09.198	•		
	page 111; column 1; ref. no	. 150999		TECHNICAL FIELDS SEARCHED (Int. Cl.4)
8	* abstract *		1	SEARCHED (IIII. CL4)
			-	D06P5/00
		*		
		:		41
	**	•		
		1.00		
	×		•	
		.*		·
	·			
	*		- 8-	
•				
		* x		
			_	
	The present search report has been d			
	Place of search	Date of completion of the search		Examiner
	THE HAGUE	26 FEBRUARY 1990	DEL	ZANT J-F.
	CATEGORY OF CITED DOCUMENTS ricularly relevant if taken alone	T: theory or princ E: carlier patent t after the filing	locument, but pub date	lished on, or
do	rticularly relevant if combined with another cument of the same category	D : document cité L : document cité	for other reasons	
A: tec	chnological background on-written disclosure	&: member of the		In acceptanting